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13. ABSTRACT (Maximum 200 words) High Sensitivity Absorption Spectroscopy (HSAS) was used to study the C <sub>2</sub> radical density in a hydrogen deficient Chemical Vapor Deposition (CVD) system for growing nanocrystalline diamond films. This work was performed in a collaboration between the University of Wisconsin group (supported by ARO) and Dr. Gruen's group at Argonne National Laboratory. The C <sub>2</sub> radical density is important because it is the likely growth specie in the hydrogen deficient growth environment. The C <sub>2</sub> radical density was measured over large range of parameter space in the CVD reactor. Research on the power balance of the plasma in the CVD reactor was performed. A microwave interferometer is being used to measure electron densities. Concentrations of benzene, C <sub>6</sub> H <sub>6</sub> , far higher than predicted by models of diamond CVD systems have been detected. This discovery is an important step toward a more quantitative understanding of the carbon balance of diamond CVD systems. We have extended the HSAS technique for use in a Reflection-Absorption mode to study molecules physisorbed on metal surfaces. The heterogenous chemistry and surface physics of many CVD, semiconductor etching, and other plasma processing systems are poorly understood. New in-situ surface diagnostics are needed to advance the understanding of the surface science of these important systems. The Ultraviolet Reflection-Absorption Spectroscopy (UVRAS) method has important advantages for in-situ studies of processing environments. It has sensitivity to a small fraction of a monolayer. This high sensitivity is due to the fact that the oscillator strengths of electronic transitions in the UV are much larger than the oscillator strengths of vibrational transitions in the infrared which are probed using competing techniques. Optical techniques have a major advantage over many other surface diagnostics, such as electron spectroscopies, in that optical techniques do not require ultra high vacuum techniques and can be used under processing conditions.				
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Two major tasks were defined in our proposal entitled "Spectroscopic Studies of Diamond Growth". One of the tasks was the study of unconventional "hydrogen deficient" diamond film Chemical Vapor Deposition (CVD) systems. Hydrogen is typically 99% by volume of the feed gas in conventional "hydrogen rich" diamond film CVD systems. Conventional CVD systems grow polycrystalline films with micron sized crystals. Hydrogen is about 1% by volume of the feed gas in unconventional "hydrogen deficient" diamond film CVD systems. Hydrogen deficient CVD systems grow polycrystalline films with very small nanometer sized crystals. The films are very much smoother than the films grown in hydrogen rich CVD systems. The smoother, nanometer scale polycrystalline films are promising for use in tribological applications and for use in thermal management applications.

The different film morphology is at least in part due to a different CVD chemistry. The carbon dimer,  $C_2$ , is thought to be the key growth specie in the hydrogen deficient CVD system. The methyl radical,  $CH_3$ , is the key growth specie in hydrogen rich CVD systems. The hydrogen deficient CVD chemistry requires a feed gas mix which is mostly an inert gas, Ar, and a carbon source such as a Buckminster Fullerene,  $C_{60}$ . Methane can also be used as a carbon source in unconventional CVD systems. This unconventional diamond film CVD chemistry was discovered by Dr. Dieter Gruen and collaborators at Argonne National Lab. We proposed a collaboration with Dr. Gruen's group at Argonne National Laboratory.

During the period covered by this report we were able to achieve several important milestones. Three years ago we reported observing the  $C_2$  radical using absorption spectroscopy in a microwave plasma similar to that used to grow the nanometer scale polycrystalline films<sup>1</sup>. This work was performed in our own laboratory at the Univ. of Wisconsin-Madison. This initial success convinced us that our High Sensitivity Absorption Spectroscopy (HSAS) experiment has the necessary sensitivity for detailed studies of the hydrogen deficient diamond CVD chemistry. We then established a very active collaboration with Dr. Gruen's group at Argonne National Lab. The HSAS experiment was moved to Argonne National Lab and our most experienced graduate student, Amanda Goyette, started working part (50-80%) time at Argonne Lab. Progress in understanding the unconventional hydrogen deficient system has been substantial. We discovered that  $C_2$  Swan band emission is directly proportional to the Swan band absorption under hydrogen deficient growth conditions.<sup>2</sup> This discovery provides a greatly simplified technique for monitoring  $C_2$  densities in CVD systems for nanocrystalline diamond growth. We also completed a major study of  $C_2$  densities over large range of parameter space in a CVD reactor.<sup>3</sup>

We also had a microwave interferometer for electron density measurements built. We tested the interferometer using a well diagnosed discharge plasma. Unlike Langmuir probes, interferometers are useful for electron density measurements in highly reactive diamond CVD systems with high gas densities. Electron density measurements were performed on the reactor at Argonne National Lab.

Simple techniques for measuring the translational or gas kinetic temperature in processing plasmas are important because an accurate determination of the gas kinetic temperature is an important piece of the power balance. Spectroscopic techniques are most useful in high reactive plasmas. We extended some of our earlier work in such techniques.<sup>4</sup>

We discovered that benzene,  $C_6H_6$ , is present in diamond CVD reactors at far higher

concentrations than predicted by models.<sup>5</sup> This discovery is an important step toward a more complete understanding of the carbon balance of diamond CVD reactors.

The HSAS technique, which we developed at the University of Wisconsin under ARO sponsorship, has been useful in studying a variety of reactive CVD and other glow discharge environments. Absorption spectroscopy using detector arrays has far greater sensitivity than older experiments using a single channel, sequentially scanned spectrometer. Low frequency noise and drifts in continuum sources often limited the sensitivity of single channel, sequentially scanned absorption experiments. The simultaneous detection of all spectral channels across an absorption feature using a detector array eliminates the effect of non quantum noise or drifts. Photon statistical fluctuations are then the primary limit on the sensitivity of the absorption experiment. The array detector makes it possible to efficiently accumulate good photon statistics. Sensitivities to fractional absorptions of 0.00001 are now routine at wavelengths from the vacuum ultraviolet to the near infrared. These recent application in diagnosing plasmas for both etching and deposition are described in our Invited Review Article.<sup>6</sup> The simplicity and sensitivity of absorption spectroscopy using detector arrays at wavelengths from the near infrared to the vacuum ultraviolet should have another major application.

The second major task in our proposal was the development of new, highly sensitive, in-situ surface diagnostics for material processing systems and for other applications. Almost all existing surface diagnostics, capable of providing microscopic information, require ultra-high vacuum conditions and thus are not applicable to processing conditions. During the last two years we developed an important new surface diagnostic, Ultraviolet Reflection-Absorption Spectroscopy (UVRAS) and we demonstrated the sensitivity of the technique during studies of benzene,  $C_6H_6$ , physisorbed on various metal surfaces.

The heterogenous chemistry and surface physics of many CVD, semiconductor etching, and other plasma processing systems are poorly understood. Almost all existing surface diagnostics, capable of providing microscopic information, require ultra-high vacuum conditions and thus are not applicable to processing conditions. New in-situ surface diagnostics are needed to advance the understanding of the surface science of these important systems. The Ultraviolet Reflection-Absorption Spectroscopy (UVRAS) method, which we developed, has important advantages for in-situ surfaces studies in processing environments. The UVRAS method is a derivative of our HSAS method. It has sensitivity to a small fraction of a monolayer. This high sensitivity is due to the fact that the oscillator strengths of electronic transitions in the UV are much larger than the oscillator strengths of vibrational transitions in the infrared which are probed using competing techniques. Optical techniques have a major advantage over many other surface diagnostics, such as electron spectroscopies, in that optical techniques do not require ultra high vacuum techniques.

To perform our initial experiments with well-understood, reproducible conditions, we use an ultra-high vacuum surface science chamber at the Synchrotron Radiation Center in Stoughton, Wisconsin<sup>7,8</sup>. This chamber is equipped with an Ar ion gun for sputter cleaning of the metal surface, a cylindrical mirror analyzer (CMA) for electron spectroscopy, and provisions for sample heating and cooling. Synchrotron radiation and the CMA allow us to perform X-ray photoelectron spectroscopy (XPS) to examine surface cleanliness. The base pressure of the chamber is  $5 \times 10^{-10}$  Torr.

We have performed UVRAS in the 250 nm range on the  $^1A_{1g} - ^1B_{2u}$  electronic transition of  $C_6H_6$  molecules physisorbed on a gold (Au) surface.<sup>7</sup> In our first experiment we observed

spectral feature or linewidths as narrow as  $100\text{ cm}^{-1}$ . These relatively narrow spectral linewidths are important in estimating the ultimate sensitivity of UVRAS. It should be possible to detect less than  $10^{-3}$  monolayer using UVRAS.

In a second experiment we studied  $\text{C}_6\text{H}_6$  molecules physisorbed on a Au, Ag, and Cu surfaces. We also modeled the UVRAS signals using solutions to Maxwell's equations in lossy thin films on lossy substrates.<sup>8</sup> Excellent agreement was obtained between the results of the model and the experimental spectra. The generally high losses of substrates in the ultraviolet is one of the physical phenomena which enhances the sensitivity of UVRAS. Benzene molecules sit parallel to the surface when physisorbed. The  $^1\text{A}_{1g} - ^1\text{B}_{2u}$  electronic transition interacts with light polarized in the plane of the ring. If the substrate were a perfect reflector then the tangential, or in plane component, of the electric field would vanish near the surface. The losses of common substrates in the ultraviolet results in significant tangential electric fields and good sensitivity to physisorbed  $\text{C}_6\text{H}_6$  molecules.

We anticipate that the UVRAS technique will enable researchers to study molecules and free radicals physisorbed on surfaces during processing conditions and that it will become an important surface science diagnostic. We are also optimistic that UVRAS will solve certain technical problems of interest to the Army.

#### Refereed Publications:

<sup>1</sup> A. N. Goyette, Y. Matsuda, L. W. Anderson, and J. E. Lawler, "C<sub>2</sub> Column Densities in H<sub>2</sub>/Ar/CH<sub>4</sub> Microwave Plasmas", J. Vac. Sci. Technol. A **16**, 337-340 (1998).

<sup>2</sup> A. N. Goyette, J. E. Lawler, L. W. Anderson, D. M. Gruen, T. G. McCauley, D. Zhou, and A. R. Krauss, "C<sub>2</sub> Swan Band Emission Intensity as a function of [C<sub>2</sub>]", Plasma Sources, Science, and Technology **7**, 149-153 (1998).

<sup>3</sup> A. N. Goyette, J. E. Lawler, L. W. Anderson, D. M. Gruen, T. G. McCauley, D. Zhou, and A. R. Krauss, "Spectroscopic Determination of Carbon Dimer Densities in Ar/H<sub>2</sub>/CH<sub>4</sub> and Ar/H<sub>2</sub>/C<sub>60</sub> Microwave Plasmas for Nanocrystalline Diamond Synthesis", J. of Physics D: Applied Physics **31**, 1975-1986 (1998).

<sup>4</sup> A. N. Goyette, J. R. Peck, Y. Matsuda, L. W. Anderson, and J. E. Lawler, "Experimental comparison of rotational and gas kinetic temperatures in N<sub>2</sub> and He/N<sub>2</sub> discharges," J. Phys. D: Appl. Phys **31**, 1556-1564 (1998).

<sup>5</sup> A. N. Goyette, L. W. Anderson, J. R. Peck, and J. E. Lawler, "Measurement of C<sub>6</sub>H<sub>6</sub> Densities in a Diamond Deposition System", J. Chem. Phys. **110**, 4647-4650 (1999).

<sup>6</sup> L. W. Anderson, A. N. Goyette, and J. E. Lawler, "Uses of High Sensitivity White Light Absorption Spectroscopy in Chemical Vapor Deposition and Plasma Processing", invited review on "Fundamentals of Plasma Chemistry"--special volume of the series Advances in Atomic, Molecular, and Optical Physics **43**, 295-339 (2000)..

<sup>7</sup> J. R. Peck, X. L. Peng, L. W. Anderson, and J. E. Lawler, "UV Reflection-absorption Spectroscopy of C<sub>6</sub>H<sub>6</sub> on Au", Chem. Phys. Lett. **318**, 476-480 (2000).

<sup>8</sup> X. L. Peng, J. R. Peck, L. W. Anderson, C. J. Goebel, and J. E. Lawler, "Ultraviolet Reflection-Absorption Spectroscopy of Benzene on Metal Surfaces", J. Appl. Phys. **88**, 4097 (2000).